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Application of the seed-film method for the preparation of structured molecular sieve catalysts

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Abstract

The seed-film method has been applied for the preparation of various materials of potential interest as structured molecular sieve catalysts. The method has proven to be very flexible and allows for the reproducible preparation of a number of molecular sieve–substrate combinations as well as the control of the materials' properties of importance in catalytic applications such as zeolite loading, film thickness, film density and crystal orientation. The preparation of thin molecular sieve films on ceramic foams, α-alumina pellets and porous alumina supports as well as various metal surfaces is described. The preparation of zoned coatings with a compositional gradient is also discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Zeolite coatings; Zeolite membrane; Structured catalyst; Composite catalyst; Zeolite film

1. Introduction

The prosperity of molecular sieve-based materials in structured catalysts is very much dependent on the development of suitable methods for the controlled and reproducible preparation of molecular sieve films on various substrates. A number of procedures for the preparation of molecular sieve films have been presented and numerous reports have been published describing the use of these procedures for the preparation of films on different substrate types [1]. A large part of this development has been aimed at preparing molecular sieve membranes, but quite a few papers and patents also deal with the preparation of other structured zeolite materials such as zeolite-covered monoliths, distillation packing materials and conventional catalyst particles covered with a molecular sieve skin [2–13]. All of these methods do, however, suffer from different disadvantages that severely limit their usefulness for the preparation of materials tailored for optimal performance in specific catalytic applications.

Perhaps, the most versatile and flexible approach for the preparation of molecular sieve films is the seed-film method in which the substrate is first surface modified in order to optimize its charge for the adsorption of a monolayer of molecular sieve seeds. The seeds are then adsorbed and grown into a continuous film on the substrate surface. One inherent advantage of this method in comparison with the direct synthesis approach currently predominant is that the various steps of the film forming process (nucleation, seeding and growth) can be independently controlled [14].

In the present contribution, the application of the seed-film method for the preparation of structured molecular sieve catalysts is described and exemplified by the preparation of thin molecular sieve films

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on ceramic foams, α-alumina pellets and membrane supports as well as various metal surfaces. Tailoring of the resulting films for applications is discussed and exemplified by the preparation of zoned molecular sieve coatings.

2. Experimental

Details on the preparation of molecular sieve films using the seed-film method have previously been described [15]. Basically, the method consists of three separate steps, as illustrated in Fig. 1. In the first step, the surface of the substrate is modified by treatment in a solution of cationic polymer molecules to render the substrate surface charge positive. Colloidal crystals of molecular sieves with a negative surface charge are then electrostatically adsorbed onto the substrate surface. In the final step, the adsorbed crystals are induced to grow into a dense and continuous film of intergrown crystals by treatment in an appropriate synthesis solution at hydrothermal conditions. The films are calcined to remove template molecules, or synthesized in the absence of organic template molecules. In each of the steps, a number of modifications can be made in order to adapt the method to the molecular sieve–substrate combination used and in order to control properties of the resulting film which may be of importance for use of the film in an intended application. Certain substrates of interest (e.g. noble metals) do not possess a surface charge sufficient for the method to be directly applicable in aqueous solution. In order to circumvent this problem, it is possible to add an additional step, preceding the ones discussed above, in which the surface is first modified by a silane such as γ-mercaptopropyltrimethoxy silane which is hydrolyzed in order to form a silicon dioxide monolayer on the surface [16,17].

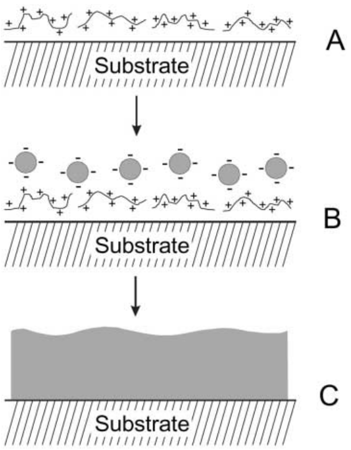

Fig. 1. Schematic of the three basic steps of the seed-film method: (A) surface charge reversal by adsorption of cationic polymer; (B) adsorption of seed crystals; (C) growth and intergrowth of crystals to form continuous film.

Characterization of the materials prepared has been carried out mainly by using scanning electron microscopy (SEM) equipped with an energy dispersive X-ray (EDX) detector, X-ray diffraction (XRD), nitrogen adsorption measurements and spectroscopic methods. Evaluation of membranes has been carried out in a Wicke–Kallenbach type permeation cell with peripheral equipment for gas flow control and analysis [18].

3. Results and discussion

The seed-film method can be used to synthesize zeolite films on a variety of supports, including silicon, quartz, alumina, coerdierite, ceramic foams, carbon, gold, platina, silver, vegetal fibers and zeolite (zoned zeolite films). Important parameters for the second step (see Fig. 1) are the size of the seed crystals, their orientation and surface coverage. The first step (surface charge reversal) and second step (adsorption of seed crystals) can be repeated in order to increase the surface coverage of the seed crystals. In the third step, the growth rate of the film and the final thickness can easily be controlled from about 100 nm and upwards by varying the synthesis time or, alternatively, by applying the method in multiple stages. Since the crystal orientation can change during the growth of the film, multiple seeding and growth steps can in some cases be adopted to control the preferred orientation. Also, additional treatments such as intensive rinsing and ultrasound treatment can be used to remove extra surface attached crystals between multiple growth stages to improve the film density in some cases.

3.1. Zeolite membranes

There has been continuing strong interest in structuring catalytic reactors with inert or catalytic

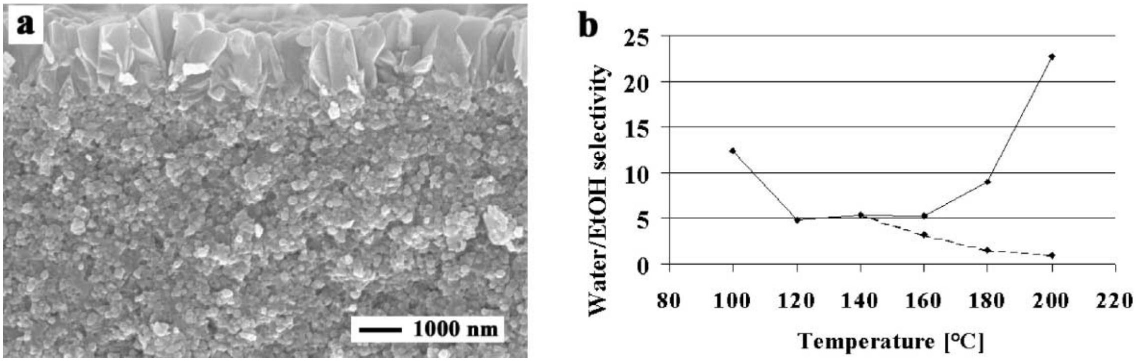

Fig. 2. Side-view of ZSM-5 membrane (a); change of separation selectivity of water–ethanol azeotrope with temperature (b); solid line is experimentally measured, whereas dashed line is a calculated separation selectivity accounting for reaction of ethanol.

membranes in order to overcome limitations in thermodynamic equilibrium and/or selectivity [19]. The commercial realizations of such processes will depend on the ability to reliably produce membranes with sufficiently high selectivities and fluxes. The application of the seed-film method for the synthesis of thin and dense supported films offers good potential [18,20–23].

Fig. 2(a) shows a SEM side-view image of a 1.5–2 μm thick aluminum rich ($Si/Al = 10$) ZSM-5 film supported on α-alumina with a surface average pore size of 100 nm [24]. Typically, templating agents become incorporated in a zeolite during synthesis and must be removed by calcination at high temperature (>400°C) to render the material useful as a membrane. However, thermal stresses during calcination can produce cracks and defects in the zeolite film. In order to eliminate the need for a high temperature pre-treatment, the membrane in Fig. 2(a) was synthesized by a method free of templating agents [25].

This membrane had to be pre-heated to about 200°C in order to free the zeolite pore system of adsorbed species such as water to obtain separation of an *n*-butane/*iso*-butane (50/50 kPa) gas mixture. The butane isomer separation selectivity ranged from a maximum of 17 at 200°C to about 5 at 400°C. The high alumina content of the ZSM-5 film made it highly hydrophilic and suitable for separating water from organic species. Fig. 2(b) shows the water/ethanol separation selectivity of the membrane as a function of temperature. A helium diluted water/ethanol azeotrope (H_2O/EtOH/He: 0.58/3.4/97 kPa) was fed to the membrane. A maximum selectivity of 13 was obtained at 100°C. At temperatures exceeding 150°C, the ZSM-5 film catalyzed the dehydration of ethanol to diethyl ether and ethylene. Based on the measured permeance of ethanol, the separation selectivity appeared to increase above 150°C (solid line), however, after accounting for the flux of reaction products from the membrane, the selectivity probably in fact decreased (dashed line).

3.2. Zeolite coatings

Conventional zeolite catalysts are produced by agglomerating fine zeolite crystals into a pellet structure with a binding material. This binder material reduces the effective external surface area of the zeolite crystals. Also, reactants and products must diffuse through this structure, to and from the zeolite crystals. A binder-free zeolite coating on a packing material would improve the accessibility of the catalyst to the reactant fluid, thus reducing mass and heat transport limitations. In fact, there has been interest in using catalytic zeolite coatings on conventional distillation column packing materials for improving flow distribution and simplifying the loading of catalyst material into the column [9]. In addition, a dense zeolite coating consisting of highly intergrown crystals could have fewer non-selective external surface sites compared to an agglomeration of fine crystals.

Fig. 3 shows SEM images of 500 nm thick ZSM-5 films produced by the seed-film method on two types of packing materials [26]. The substrate in Fig. 3(a) is

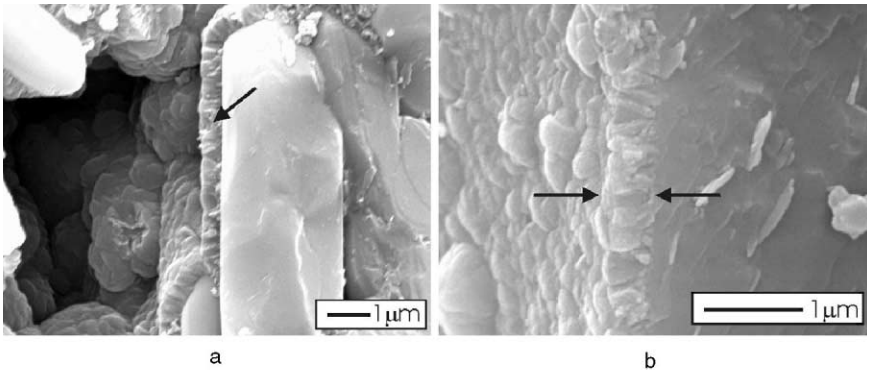

Fig. 3. SEM images showing ZSM-5 films (indicated with arrows) on a spherical pellet (a) and ceramic foam (b).

a meso- and macroporous alumina sphere (6.35 mm) and in Fig. 3(b) a highly macroporous ceramic foam ($2.5 \times 2 \times 1\,\mathrm{cm}^3$). Nitrogen adsorption measurements indicated that the specific surface areas of the spherical pellets and foams were 4.6×10^{-1} and $1.7 \times 10^{-2}\,\mathrm{m}^2\,\mathrm{g}^{-1}$, respectively. Whereas, the zeolite loadings on the spherical pellets and foams were 3.4×10^{-4} and 1.4×10^{-2} g zeolite (g substrate)$^{-1}$, respectively. The large difference in zeolite loadings obtained, despite the similar film thicknesses and specific surface areas, was due to the fact that for the spherical pellets, zeolite film which was intended only formed on the external surface and in pores close to the surface, whereas for the ceramic foams, the entire internal surface area was coated with a zeolite film. Also, for both packing materials, zeolite was predominately present in the form of a film rather than as crystal aggregates.

Catalytic material is typically applied to the internal surface of the channels of monolith supports as a washcoat with perhaps binder materials. The poor distribution of the washcoat contributes to mass transport limitations and an ineffective utilization of the catalyst [27]. With the seed-film method evenly distributed, dense and binderless zeolite coatings can be synthesized in monolith channels with a controllable coating thickness and morphology. Fig. 4(a) shows an SEM side-view image of an 800 nm thick ZSM-5 film on the macroporous internal wall of a cordierite monolith (400 cpsi). By varying the synthesis conditions and/or number of hydrothermal treatment steps, the film thickness could be varied from 110 nm to 6 µm. Fig. 4(b) shows the surface morphology of a thicker 6 µm coating which consisted of dome-like clusters of crystals. It was found that during

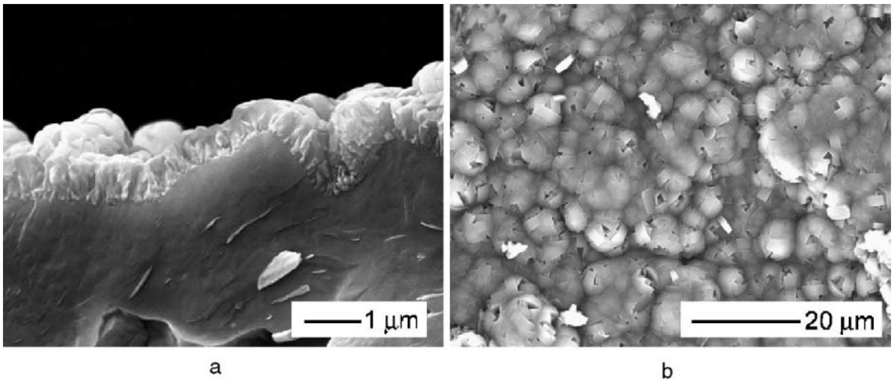

Fig. 4. Side-view of an 800 nm thick ZSM-5 film (a) and top-view of a 6 µm ZSM-5 film (b) on cordierite monoliths.

hydrothermal treatments, crystals nucleated in the synthesis solution were deposited on the film surface. These extra surface attached crystals became partially intergrown with the film. In some cases, it was estimated that these surface attached/agglomerated crystals comprised as much as 60% of the total zeolite coating. However, it was found that additional ultrasound treatments and intensive rinsing between the hydrothermal growth stages could be used to reduce the number of surface attached crystals and improve the density and compactness of the coating.

Structured reactor packing materials/catalyst supports made of stainless steel with a high chromium and nickel content are of interest because of their thermal stability and acid resistance. Metals such as stainless steel can also be conveniently fabricated into wire gauze, monoliths and other more complex designs such as open cross-flow structures consisting of superimposed corrugated sheets [28]. Using the seed-film method, thin and continuous silicalite-1 and zeolite Y films with controllable thickness have been synthesized on four types of steel supports [29]. The steel types were carbon and stainless steel with varying alloy contents. The iron content varied from about 100% for the carbon steel to as low as 54% for the stainless steel which had the highest alloy content, i.e. a very wide range of steel types were covered. The thickness of the films could be varied between 200 and 800 nm for silicalite-1 films and between 2 and 6 μm for the Y films. Continuous, crack-free and transparent films were formed on all steel types after zeolite synthesis. The type of steel did not affect the film morphology or thickness. The zeolite films on stainless steel supports were stable during calcination, although cracks were formed, whereas a thick magnetite/hematite film was formed on carbon steel upon calcination and the zeolite film vanished. The width of the cracks was dependent on the steel type. Fig. 5(a) shows a 2.2 μm zeolite Y film on a stainless steel support and Fig. 5(b) shows an 800 nm silicalite-1 film on stainless steel.

3.3. Zoned zeolite films

There has been interest in producing compositionally zoned zeolite crystals in which a ZSM-5 crystal is coated with a silicalite-1 shell [30–32]. The silicalite-1 shell could serve to eliminate the non-shape selective surface sites of ZSM-5 and/or act as a kind of membrane skin that by increasing the diffusion path length improves the selectivity of products or reactants diffusing in or out from the active zone of the crystal. This approach was used to prepare compositionally zoned MFI films [33]. First, the seed-film method was used to prepare a ZSM-5 film on a quartz substrate. Next, the growth of the film was continued with a second hydrothermal treatment, however in a synthesis solution free of aluminum. Fig. 6(a) shows an SEM side-view image of a zoned MFI film consisting of a 3.3 μm thick silicalite-1 film covering a 3.1 μm thick ZSM-5 film. An arrow in Fig. 6(a) indicates the border between the two compositional zones, which is noticeable due to a slight difference in the surface texture of the ZSM-5 and silicalite-1 regions. A line in Fig. 6(a) indicates where an EDX line scan was made on the film, the results of which are shown by the aluminum Kα and silicon Kα signals plotted in Fig. 6(b). The start of the EDX line scan at 0 μm in Fig. 6(b) corresponds to the dot in Fig. 6(a) on the quartz substrate.

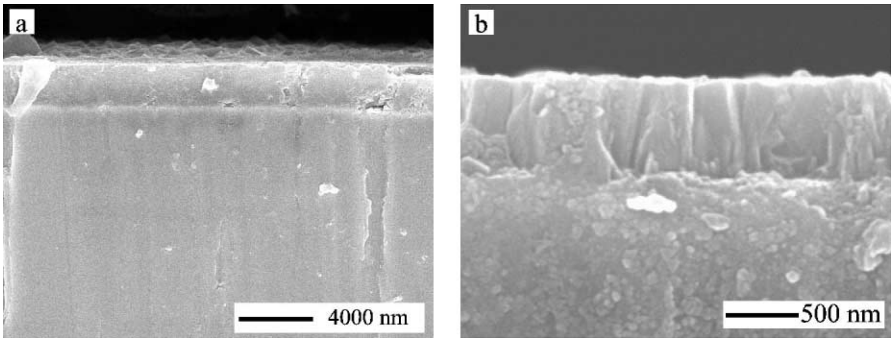

Fig. 5. Side-view images of 2.2 μm Y-zeolite (a) and 800 nm silicalite-1 (b) films on stainless steel.

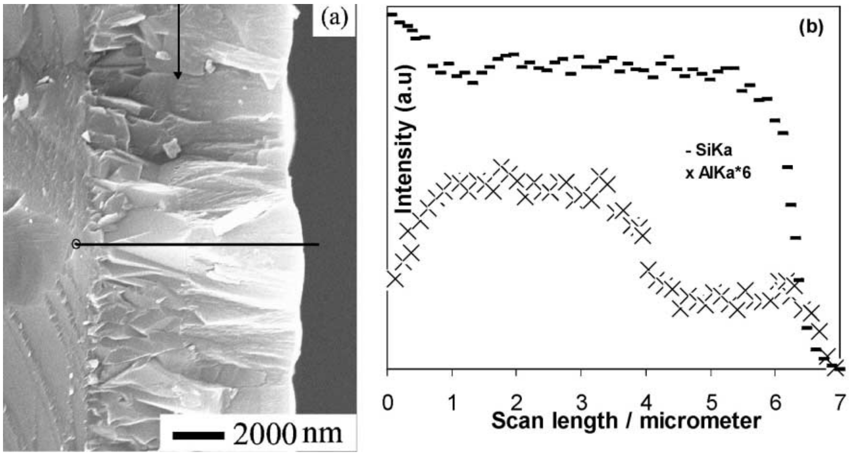

Fig. 6. Side-view image of zoned zeolite film of silicalite-1 on ZSM-5 (a) and EDX line scan of zoned film (b).

The Al signal from the support and the silicalite-1 film is not zero due to the background signal. The Al signal decreases abruptly after about 3 μm at about the position of the border between ZSM-5 and silicalite-1 layers. The EDX analysis indicated that the ZSM-5 layer was aluminum-rich with a Si/Al ratio of about 10. XRD analysis indicated that the crystals of the silicalite-1 layer predominately adopted the preferred orientation of the crystals of the ZSM-5 film rather than the orientation normally observed for silicalite-1 films prepared by the seed-film method. This indicated that the silicalite-1 layer probably formed due to the continued growth of the crystals of the ZSM-5 layer instead of nucleation of new silicalite-1 crystals on top of the ZSM-5 film. This is also supported by the fact that many of the crystal contour lines continue across the compositional gradient in Fig. 6(a). The practical implications of this finding is that the zoned film perhaps consists of a continuously propagating microporous channel system joining the zoned regions that is free of additional diffusion resistances imposed by crystal boundaries.

4. Conclusions

The versatility of the seed-film method was demonstrated by its use for preparing zeolite coatings on a range of materials suitable as reactor packings and catalyst supports including alumina pellets, ceramic foams and steel. These zeolite coatings are characterized as dense compact films consisting of highly intergrown crystals rather than crystal aggregates. The basic seed-film method has been successfully adapted for each substrate–zeolite combination and it can be used to produce coatings with a controllable thickness and morphology. It has also been used to produce thin films on porous α-alumina supports that are sufficiently defect-free to be used as membranes for isomer separation. They can be catalytically active and thus have a potential for applications as catalytic membranes. Finally, zoned MFI coatings have been prepared with sharp compositional gradients and consisting of fully intergrown crystals of ZSM-5 and silicalite-1.

Acknowledgements

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